



## Review

# The NO/NO<sub>x</sub> ratio effect on the NH<sub>3</sub>-SCR efficiency of a commercial automotive Fe-zeolite catalyst studied by operando IR-MS

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## ARTICLE INFO

## Article history:

Received 10 May 2011

Received in revised form

11 November 2011

Accepted 15 November 2011

Available online 23 November 2011

## Keywords:

Automotive depollution

NO<sub>x</sub> removal

NH<sub>3</sub>-SCR

Fe-zeolite

Operando

Ammonium nitrate

NO/NO<sub>x</sub> ratio

## ABSTRACT

A commercial zeolite-based catalyst for NO<sub>x</sub> removal via ammonia SCR was studied with either pure NO or pure NO<sub>2</sub> (as NO<sub>x</sub> compounds). The SCR efficiency was greatly enhanced when using pure NO<sub>2</sub>. The CO conversion levels enabled to illustrate that NO<sub>2</sub> favours the CO oxidation into CO<sub>2</sub>, while NO formed would participate in the fast SCR path (like a 'masked' fast SCR process). The formation of NH<sub>4</sub>NO<sub>3</sub> at low temperature, when using pure NO<sub>2</sub>, and its deposit onto the catalyst was evidenced by mean of the IR operando methodology. Its accumulation leads to a loss of activity for the NO<sub>x</sub> reduction, which must certainly be associated to an obstruction of the microporous system. Nevertheless, after a single thermal regeneration of the catalyst (which would arise during the catalyst 'real life' upon any increase of the engine regime), the SCR efficiency was fully recovered.

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## 1. Introduction

Air pollution occurs when any substance present in the atmosphere reaches a concentration high enough to produce a negative effect on people, animals or plants or to modify the natural ecosystems. The most important pollutants for S-free sources are carbon monoxide (CO), unburned hydrocarbons (HC), particulate matter (PM) and nitrogen oxides (NO<sub>x</sub>) [1–3]. The major source of air

contaminants comes from the combustion processes, where the transport sector lies at a prominent position, notably in urban areas [4,5]. Car manufacturers are pushed, by severe regulations, to decrease the environmental impact of the exhaust gases and as a consequence lean-burn engines have been developed. These compression ignition engines, operating in oxygen excess conditions, achieve both the fuel consumption reduction and the CO<sub>2</sub>, CO and unburnt HCs emissions lowering. However, the NO<sub>x</sub> level at the engine outlet remains too high [6].

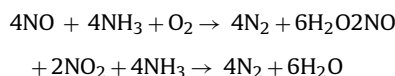
Different deNO<sub>x</sub> aftertreatments have thus been developed, but it seems that the Selective Catalytic Reduction (SCR) is one the most promising solution. This process has been studied

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in-depth for its application to  $\text{NO}_x$  removal in stationary sources [7–9], being the best solution. Even, the ammonia SCR has been chosen by the European HD (Heavy-Duty) vehicle manufacturers as the technology to achieve the European standards emissions [10] and nowadays it is under study for application in passenger cars. In the literature, a great variety of SCR-materials can be found: for example the well-known Ti-based catalysts [11,12] or the Ag– $\text{Al}_2\text{O}_3$  compounds [13–16]. More recently, zeolite-based catalysts were reported to be effective for the selective catalytic reduction of NO with methane or propene [17–19]. In particular, Fe-containing zeolites present a significant efficiency for the  $\text{NO}_x$  SCR with either hydrocarbons or ammonia as the reducing agent [20–22].

A literature survey indicates that the SCR mechanism depends on the nature of the catalyst [23]. Long and Yang [24] show indeed that the reactivity of pre-adsorbed  $\text{NH}_4^+$  on Fe-ZSM5 depends on the  $\text{NO}/\text{NO}_2$  ratio, decreasing in the order  $\text{NO} + \text{NO}_2 > \text{NO}_2 \gg \text{NO}$  and they proposed  $\text{NO}_2(\text{NH}_4^+)_2$  as an intermediate active species. However, some discrepancies appear in the literature and for example, Kiovisky et al. [25] found that H-MOR is more reactive when  $\text{NO}_2$  is in excess in the  $\text{NO}_x$  mixture, while Brandin et al. proposed  $\text{NO}^+$  as an intermediate [26]. Some other publications point out that  $\text{NO}_2$  would be required for the fast SCR



[27–30] but its amount also depends on the conditions and the used catalyst. For instance, Schwidder et al. [31] demonstrate that for a Fe-ZSM5 catalyst, the NO oxidation is slower than the NO reduction thus enabling them to exclude free  $\text{NO}_2$  produced by NO oxidation as an intermediate for the standard SCR reaction.

Furthermore, the majority of the investigations use a model mixture of gases where only  $\text{NO}_x$ ,  $\text{O}_2$  and  $\text{NH}_3$  are sent to the catalyst [24–31].  $\text{H}_2\text{O}$  is sometimes added to the mixture and consequently the results are affected [32] as expected from either thermodynamic (mass action law applied to water being a SCR product) or kinetic considerations both including a possible water competitive adsorption onto the active sites. Car manufacturer industry is however more and more interested in the study of the reaction in conditions as close as possible to the real application, i.e. when the commercial catalyst reduces the  $\text{NO}_x$  in presence of  $\text{NH}_3$ ,  $\text{O}_2$ , but also  $\text{H}_2\text{O}$ , HC,  $\text{CO}_2$  and CO as the main exhaust components. It seems to be accepted by the scientific community that the presence of  $\text{NO}_2$  in the mixture promotes the de $\text{NO}_x$  activity of Fe-based zeolite catalysts, but the possible formation of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) in the low temperatures range and its links with  $\text{NO}_2$  presence make this study difficult. Indeed, the deposition of a white powder was reported at temperatures below 500 K but this powder was not really detected on the catalyst surface, so a debate persists regarding the  $\text{NH}_4\text{NO}_3$  formation whether from a catalytic effect or from a parallel gas phase reaction [31].

The present paper reports the study of the SCR activity of a commercial Fe-zeolite based catalyst (supplied by Renault car company) under different  $\text{NO}/\text{NO}_x$  ratios and simulating a real exhaust gases mixture made of a rather low concentration of  $\text{NO}_x$  together with  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , CO and  $\text{NH}_3$  as the reducing agent. This study was conducted using an operando IR-MS system that enables the time-resolved analysis of both the gas phase and the catalytic surface under operating conditions. New information about the formation of  $\text{NH}_4\text{NO}_3$  onto the catalyst and its deactivation were thus obtained giving a further contribution to the knowledge of the  $\text{NH}_3$ -SCR process.

## 2. Experimental

### 2.1. Samples

The catalysts used for this study are made of the active phase of real monoliths which were supplied by Renault. More precisely, the samples come from the removal of the wash-coat from a cordierite based honeycomb using a  $\text{N}_{2\text{liq}}$  treatment that consists in successive quenches of the samples into liquid nitrogen, followed by further room temperature ultrasonic treatments. These physical extreme conditions provoke stress and strain phenomena on the material until its detachment from the monolith, without modifying its morphology nor its chemical composition or crystalline zeolitic structure, as checked by ICP AES and XRD measurements.

The two studied samples are thus composed of a mixture of Fe-containing ZSM-5 zeolite and alumina binder. They are labelled as Fresh catalyst and Aged catalyst (fresh catalyst after an ageing treatment). The ageing consisted of a hydrothermal treatment of 24 h at 750 °C in presence of 10% of  $\text{H}_2\text{O}$ .

### 2.2. Reaction system (operando)

The operando system, whose sketch is described in previous publications [33,34], allows the study of the catalyst under working conditions. The flow set-up and the gas mixture are already described [35] and also the reactor cell [22,34].

The conditions for the operando experiments were established at  $\text{GHSV} = 120,000 \text{ h}^{-1}$  (which would correspond to a monolithic GHSV around  $30,000 \text{ h}^{-1}$  according to an empirical factor 4 taking into account the void volume in a monolith). In order to keep constant the GHSV, the total flow was adjusted depending on the mass of the disc (the mass was always close to 15 mg with a total flow around  $30 \text{ mL min}^{-1}$ ). The catalytic surface is analysed by FTIR and the outlet gases by Mass Spectrometer and FTIR-gas.

The gas composition for the SCR study was established as follows: 150 ppm of  $\text{NO}_x$  ( $\text{NO}/\text{NO}_x = 1$  and 0) + 180 ppm  $\text{NH}_3$  + 14%  $\text{O}_2$  + 4%  $\text{CO}_2$  + 300 ppm CO and 1%  $\text{H}_2\text{O}$  in Ar. Different temperatures were tested between 165 °C and 400 °C. The NO and the  $\text{NH}_3$  oxidation capacity of both catalysts were tested also by operando methodology. A flow made of (1000 ppm NO + 14%  $\text{O}_2$ ) or (180 ppm of  $\text{NH}_3$  + 14%  $\text{O}_2$ ), respectively was sent to the catalysts at different temperatures.

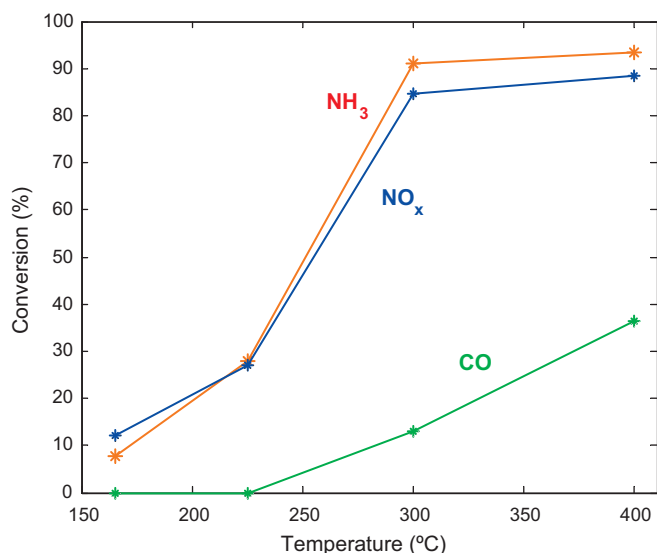
A Thermo-Programmed-Desorption experiment (TPD) was conducted from 165 °C to 400 °C (in pure Ar, 2 °C/min).

## 3. Results and discussion

### 3.1. SCR with different $\text{NO}/\text{NO}_x$ ratio

With the aim to characterize solely the different reactivity of NO and  $\text{NO}_2$  in the  $\text{NH}_3$ -SCR, the same  $\text{NH}_3/\text{NO}_x$  ratio and the same total  $\text{NO}_x$  amount were always applied during all the experiments described in this work. The concentrations of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and CO were also kept constant and we used either pure NO or pure  $\text{NO}_2$  in the mixture in order to analyse the catalyst behaviour. Pure  $\text{NO}_2$  is for sure not representative of the  $\text{NO}_x$  at the engine out, and even if a Diesel Oxidation Catalyst (DOC) is present between the engine and the SCR block, the  $\text{NO}_2$  contribution to  $\text{NO}_x$  species at the inlet of the de $\text{NO}_x$  catalytic honeycomb is most often below 80%. However, for a comprehensive study, we decided to simplify the system by comparing the pure NO and pure  $\text{NO}_2$  removal efficiency.

The conversion results obtained with the aged catalyst (which is most representative of an on-board catalyst) are plotted as a function of the temperature in Fig. 1. Under a slight ammonia excess regarding stoichiometry ( $\text{NH}_3/\text{NO}_x = 1.2$ ), when the  $\text{NO}_2/\text{NO}_x$  ratio was set to



**Fig. 1.** Conversion of NO<sub>x</sub>, NH<sub>3</sub> and CO during SCR with NO<sub>2</sub>/NO<sub>x</sub>=0 and NH<sub>3</sub>/NO<sub>x</sub>=1.2 over the aged catalyst.

zero the NO<sub>x</sub> conversion was high: >90% at 400 °C and 300 °C. However, a big decrease between 225 °C and 300 °C must be noticed: the NO<sub>x</sub> conversion at low temperature is lower than 30% and it drops to nearly 10% at the lowest tested temperature, i.e. 165 °C. If we compare with some results found in the literature using also Fe-zeolite based system, we can notice that the profile of NO<sub>x</sub> and NH<sub>3</sub> conversion is similar: high deNO<sub>x</sub> activity at high temperatures with an opposite trend at low temperature. However, in our case the inflexion point lies around 275 °C, while it was observed at higher temperatures in the literature (around 325–350 °C) [32]. This different de-NO<sub>x</sub> activity is even more important when comparing the data with the ones obtained using vanadium-based catalysts reported also by Grossale et al. [36].

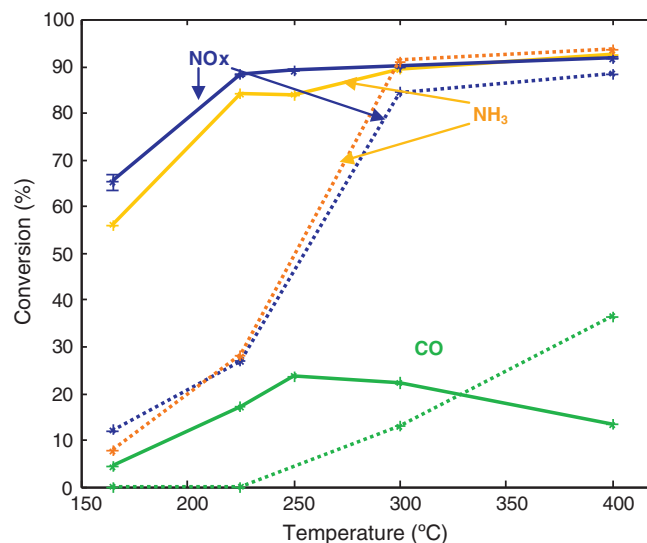
When comparing both ammonia and NO conversions, we observe above 225 °C a deviation from the pure SCR stoichiometry which is characterized by a NH<sub>3</sub> conversion higher than that of NO. More precisely, according to the SCR stoichiometry with NO:



One would expect higher NO conversion than NH<sub>3</sub> due to the NH<sub>3</sub>/NO=1.2 ratio. The fact that an opposite trend was found (higher NH<sub>3</sub> conversion) indicates that NH<sub>3</sub> oxidation also takes place, especially in the high temperature range. Starting from the hypothesis that NH<sub>3</sub> is mainly oxidized into N<sub>2</sub>, we find that in the high temperature range (300–400 °C), around ≈20% of ammonia is not used for the SCR of NO. On another hand, hypothesizing a selective oxidation of ammonia into NO<sub>x</sub> species, the part of NH<sub>3</sub> not involved in the SCR process drops to around ≈10%. Such an over-consumption was previously described in the literature [37] but was not observed with other type of catalysts [38].

Regarding the CO oxidation, the conversion is only important in the high temperature range (around 35% at 400 °C), being even negligible below 300 °C. Regarding the selectivity, the possible N<sub>2</sub>O product is never detected over the whole temperature range which makes the catalyst 100% selective to N<sub>2</sub>.

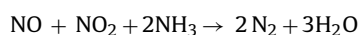
In order to study the reactivity of the SCR system in presence of NO<sub>2</sub>, the same experimental conditions were applied except a ratio NO<sub>2</sub>/NO<sub>x</sub>=1 (150 ppm NO<sub>2</sub>). The results are presented on Fig. 2 (full line) and compared with those obtained from a ratio NO<sub>2</sub>/NO<sub>x</sub>=0 (previous results, dotted line). For the temperature range below 300 °C, a pronounced NO<sub>x</sub> conversion increase was observed when using pure NO<sub>2</sub>. Again, no N<sub>2</sub>O production was detected and the

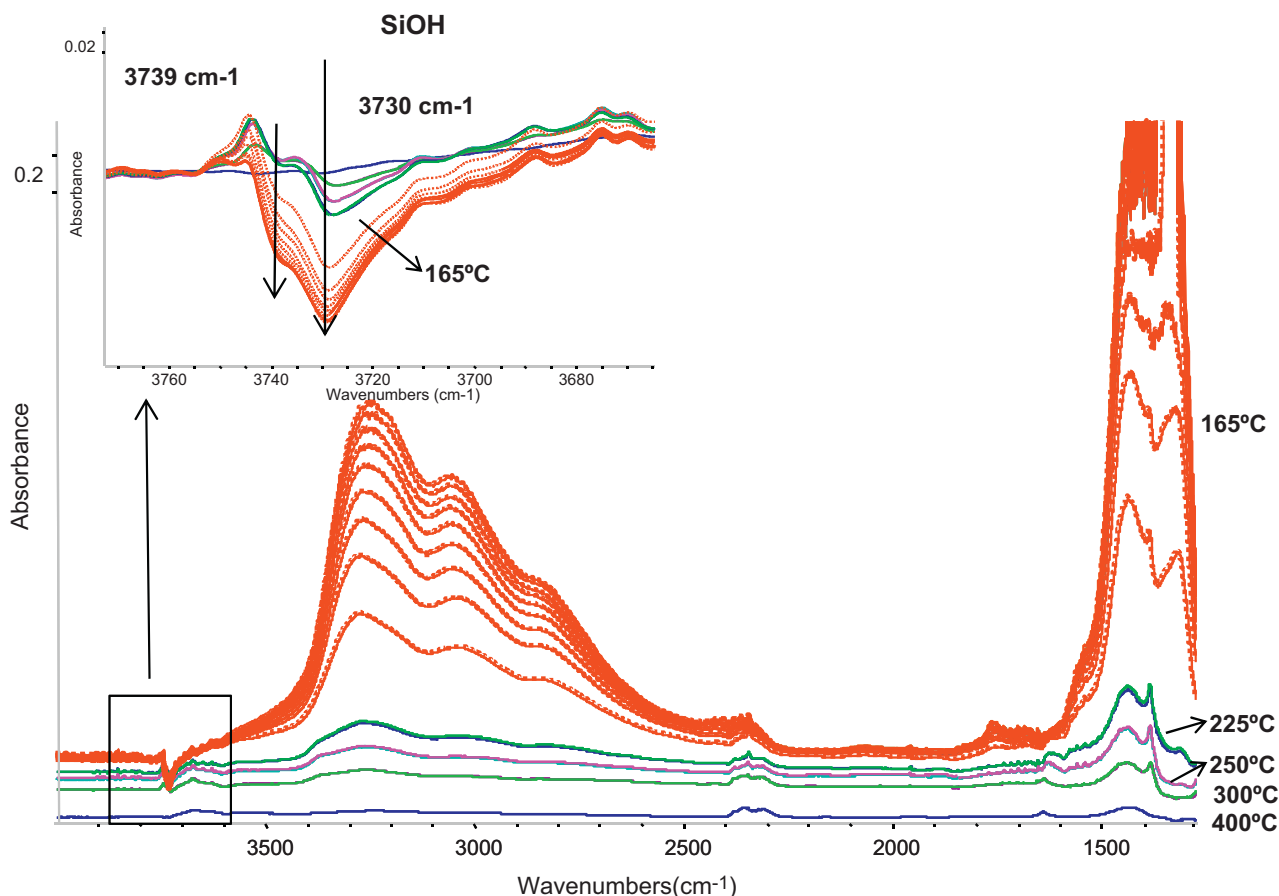


**Fig. 2.** Conversion of NO<sub>x</sub>, NH<sub>3</sub> and CO versus temperature, during SCR with NH<sub>3</sub>/NO<sub>x</sub>=1.2 and NO<sub>2</sub>/NO<sub>x</sub>=0 (dotted line) or NO<sub>2</sub>/NO<sub>x</sub>=1 (full line) over the aged catalyst.

catalyst remains 100% N<sub>2</sub> selective. Indeed, when pure NO<sub>2</sub> is present in the flow, the NO<sub>x</sub> conversion reaches values above 60% in the whole temperatures range. In general, the literature data indicate that a NO/NO<sub>x</sub>=0.5 mixture leads to the maximum activity [24], while here we report that even with 100% of NO<sub>2</sub> in the mixture the deNO<sub>x</sub> activity is highly improved. Devadas et al. [39] also found that NO<sub>2</sub> in the feed drastically enhanced the NO<sub>x</sub> removal efficiency and that this effect was more pronounced at low temperatures. They described this behaviour as a special feature of the Fe-ZSM5 structure which enables to keep a high activity level even with pure NO<sub>2</sub>. On another hand, Colombo et al. [40] showed that a Cu-zeolite which possesses a high ammonia storage capacity and ammonia oxidation activity is less sensitive to the NO<sub>2</sub> feed content regarding its deNO<sub>x</sub> efficiency.

Coming back to the data from Fig. 2, as pure NO leads to lower deNO<sub>x</sub> conversion than pure NO<sub>2</sub>, it suggests that the NO to NO<sub>2</sub> oxidation would be the rate-determining step, at least in the temperature range below 300 °C. The NO to NO<sub>2</sub> oxidation capacity of the catalysts will thus have to be analysed in a next step of this work. Moreover, the NH<sub>3</sub> conversion is close to the NO<sub>x</sub> conversion above 300 °C, indicating that a residual NH<sub>3</sub> oxidation occurs (the flow being always ammonia rich). For lower temperatures, and especially when NO<sub>2</sub> is used, the NH<sub>3</sub> oxidation part decreases (NH<sub>3</sub> conversion < NO<sub>x</sub> conversion). As the NO<sub>2</sub> molecule possesses a higher oxidizing power than NO, this result confirms that the main contribution to the NH<sub>3</sub> oxidation does not take place in the gas phase and suggests that the NH<sub>3</sub> oxidation mechanism would go through co-adsorption of NO and NH<sub>3</sub> on the same oxidizing sites. Finally, it can be seen that pure NO<sub>2</sub> also influences the CO oxidation: it is the first experiment for which the CO conversion is over 10% in the medium range of temperatures (between 225 and 300 °C). In this case, the gas phase oxidation of CO by NO<sub>2</sub> could be a possible path, however considering the amount of converted CO (300 × 20% = 60 ppm at 250 °C) which would lead to the production of 60 ppm of NO, this hypothesis does not seem to be consistent with the NO<sub>x</sub> conversion (150 × 90% = 135 ppm converted and 15 ppm remaining) unless the formed NO participate to the SCR reaction according to the widely described fast SCR path [27,28]:





**Fig. 3.** Difference spectra of the aged catalyst during SCR with a  $\text{NO}_2/\text{NO}_x = 1$  and  $\text{NH}_3/\text{NO}_x = 1.2$  at different temperatures: 400 °C, 300 °C, 250 °C, 225 °C and 165 °C (dotted and red); notice that except at 165 °C all spectra overlap in steady state conditions (OH region zoom included). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

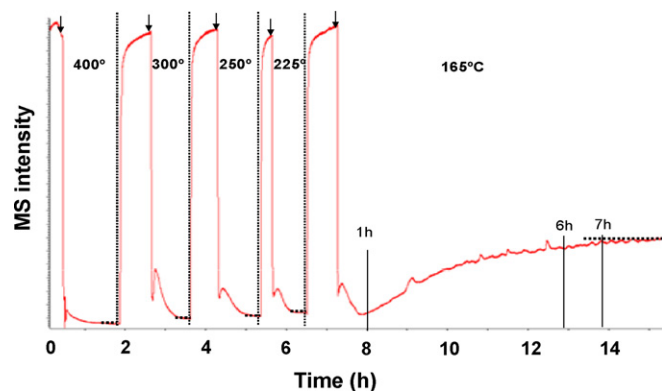
A second hypothesis, better supported by the data, lies in the availability of Fe oxidizing sites for CO oxidation, as they are no more required for the NO to  $\text{NO}_2$  oxidation step nor for the  $\text{NH}_3$  oxidation (or at least to a much smaller extent).

In order to better understand the reactivity of the catalyst associated to the presence of pure  $\text{NO}_2$ , the IR spectra of the catalyst under duty were also analysed. Fig. 3 represents some difference spectra of the surface under steady state conditions at each tested temperature (the spectrum of the surface after catalyst activation was subtracted). For any temperature above 165 °C, all the spectra acquired after different times on stream overlap and this indicates that the surface does not change anymore during the SCR reaction. A surface dynamic equilibrium state associated to steady state catalytic activity is thus reached. In general, the spectra mainly show the typical profile of  $\text{NH}_3$  adsorbed onto the catalyst in the ammonium form: the stretching modes of N–H vibrations (from  $\text{NH}_4^+$  in H-bonding interaction) appear as broad bands between 2600 and 3500  $\text{cm}^{-1}$ , while the  $\text{NH}_4^+$  anti-symmetric bending  $\delta_a(\text{NH})$  mode is centred at 1440  $\text{cm}^{-1}$ . A less intense band at 1620  $\text{cm}^{-1}$ , overlapping with the symmetric bending mode of  $\text{NH}_4^+$ , is assigned to  $\text{NH}_3$  coordinated onto metallic electron vacancies [41,24]. Simultaneously, negative bands around 3600  $\text{cm}^{-1}$  traduce the disappearance of OH groups associated to the zeolite acidic sites and thus their consumption when ammonium is formed.

The spectral evolution upon time on stream changed when the SCR reaction with pure  $\text{NO}_2$  was carried out at 165 °C. Indeed, the surface did not remain the same anymore and the continuous increase of the intensity of new bands (between 1500 and

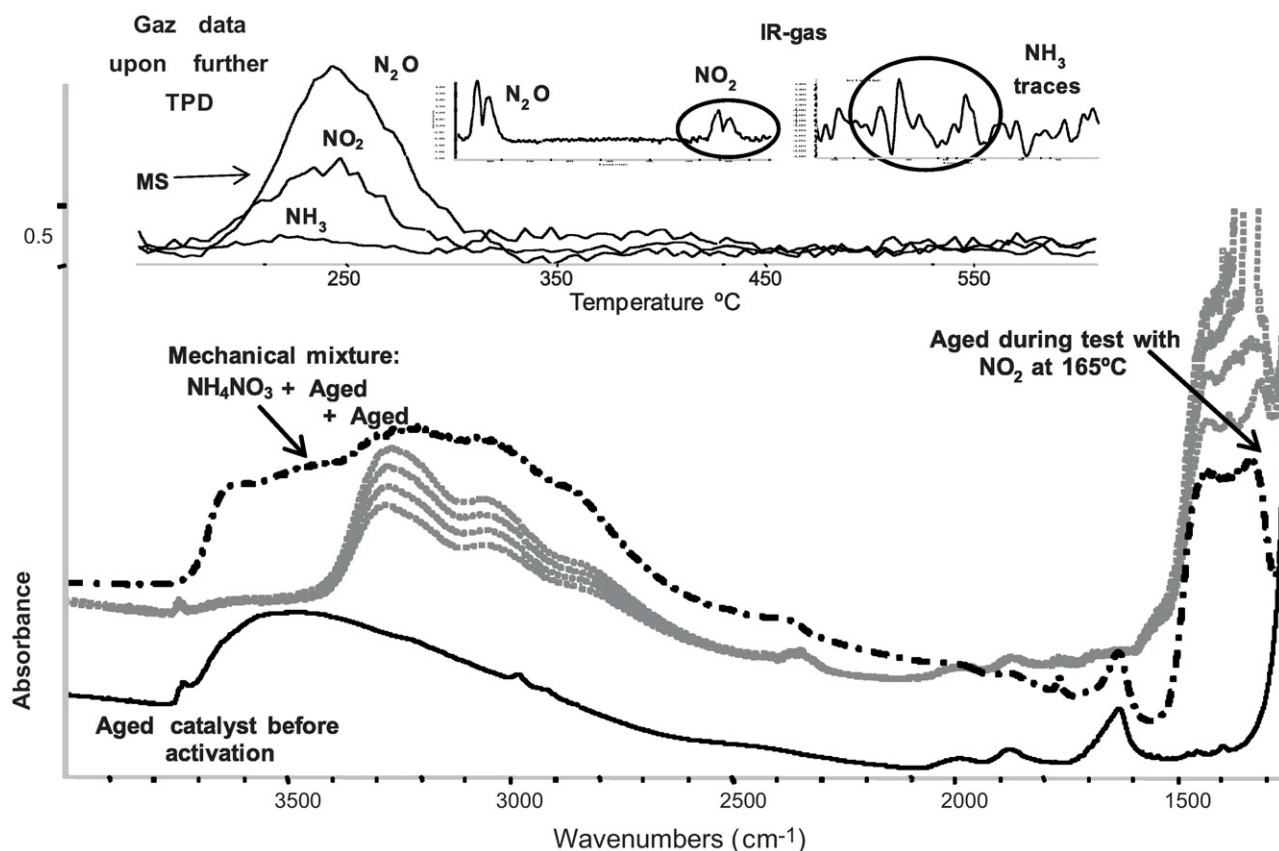
1300  $\text{cm}^{-1}$ ) indicates the accumulation of new species onto the surface. When focusing on the OH region (zoom included in Fig. 3), it can be noticed, that at 165 °C, both external and internal silanol groups, with corresponding  $\nu(\text{SiO-H})$  bands at 3739 and 3730  $\text{cm}^{-1}$ , respectively, decrease in parallel with these surface species accumulation. A deposit of these accumulating species both on the external surface and at the pore mouths (where ‘internal silanols’ are expected to be the most abundant) would thus occur.

In order to better illustrate what happens at such a low temperature, the  $\text{NO}_x$  evolution in the gas phase is reported on Fig. 4. The



**Fig. 4.** Evolution of the MS signal ( $m/z = 30$  associated to  $\text{NO}_x$ ) with time during the SCR reaction ( $\text{NO}_2/\text{NO}_x = 1$  and  $\text{NH}_3/\text{NO}_x = 1.2$ ) at different temperatures over the aged catalyst.





**Fig. 5.** Bottom part: IR spectrum of the aged catalyst before activation and reaction (thin-black), IR spectra of the aged catalyst during the test at 165 °C (dotted-grey) and mechanical mixture of  $\text{NH}_4\text{NO}_3$  and aged catalyst (dotted-black). Upper part: Gas analysis results during TPD (mass Spectrometry signal and IR-gas data).

modification with time on stream of the MS signal associated to  $\text{NO}_x$  ( $m/z = 30$ ) is given for all the tested temperatures. Between 400 and 225 °C, the experimental results are similar and obtained using the following methodology: the by-pass level of  $\text{NO}_{x\text{-inlet}}$  is first determined before switching to the catalyst (indicated by an arrow) and then the  $\text{NO}_x$  level decreases when the flow goes through the reactor. After around 30 min the reaction reaches the steady state and the conversion values for  $\text{NO}_x$  is calculated from this level.

The evolution is rather different at 165 °C: after 1 h of reaction, the  $\text{NO}_x$  level decreases to the same level as that obtained at higher temperatures, but then (between 1 and 6 h of reaction) a slow but constant increase of  $\text{NO}_{x\text{-outlet}}$  is recorded and indicates a deactivation of the catalyst. As described previously, some species simultaneously deposit onto the catalyst, indeed (Fig. 3). Finally, after 7 h under reaction stream, the  $\text{NO}_x$  level reaches a new steady state at a higher level (marked with a dotted line in Fig. 4). That level corresponds to the one taken into account for the calculation of  $\text{NO}_x$  conversion at 165 °C, which is reported on Fig. 2.

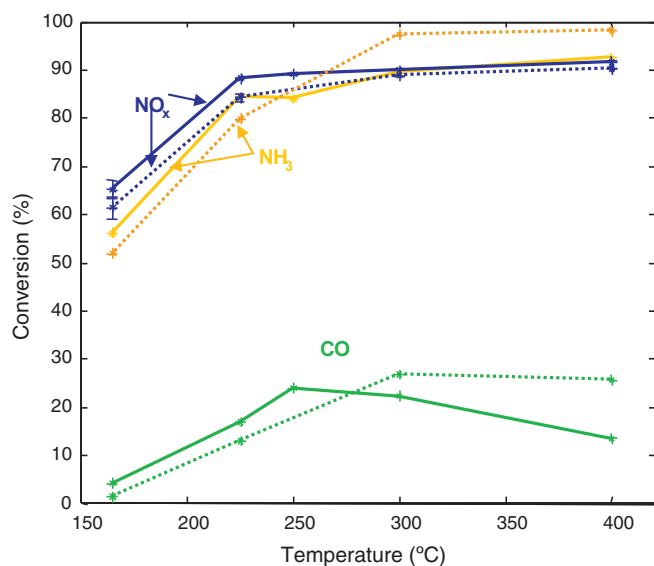
The nature of the deposit remaining on the catalytic surface at low temperature was identified as ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). Effectively, Fig. 5 illustrates various spectra obtained with/without  $\text{NH}_4\text{NO}_3$ : in dotted-grey lines some subtracted spectra of the aged catalyst during the test at 165 °C, in thin-black the spectrum of the catalyst before activation and in dotted-black a mechanical mixture of  $\text{NH}_4\text{NO}_3$  and the aged catalyst are presented. Indeed, this comparison strongly suggests that the compound formed onto the catalyst is  $\text{NH}_4\text{NO}_3$ . Ammonium nitrite ( $\text{NH}_4\text{NO}_2$ ) is another possible candidate for species accumulating onto the catalyst in the low temperature range and which would lead to similar IR vibrations.  $\text{NH}_4\text{NO}_2$  was indeed reported as the  $\text{N}_2$  selective SCR reaction intermediate, but its formation arises from the reduction of  $\text{NH}_4\text{NO}_3$  in presence of NO [42] for reaction temperatures above 200 °C [43].

In order to further confirm the nature of the deposit, a Thermo-Programmed-Desorption experiment (TPD) was realized from 165 ° to 400 °C (pure Ar, 2 °C/min) after the SCR reaction was performed at 165 °C. The analysis of the deposit decomposition (as followed by MS and IR, shown in the upper part of Fig. 5) clearly indicates the production of  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$  as the main products, together with  $\text{NO}_2$  and  $\text{NH}_3$ . These compounds are typical for the thermal decomposition of  $\text{NH}_4\text{NO}_3$  [28,32], which is consistent with our assignment of the species detected at the catalytic surface.

As a conclusion of this part, the formation of  $\text{NH}_4\text{NO}_3$  at low temperature is evidenced when using pure  $\text{NO}_2$ . This leads to a drop of the de- $\text{NO}_x$  activity, which must certainly be associated to an obstruction of the zeolitic microporous system by this ammonium nitrate deposit.

Aiming at checking the regeneration ability of the catalyst, the same experiment (SCR with a  $\text{NO}_2/\text{NO}_x = 1$  and  $\text{NH}_3/\text{NO}_x = 1.2$  at different temperatures) was performed over the sample after its reactivation during the TPD. Actually, in the case of a real catalyst located in the exhaust pipe of an automotive vehicle, the low temperature working conditions would consist in short periods (cold starts) followed by warmer ones due to the increase of the engine load. The results are plotted in Fig. 6, for both the 'as received' aged sample (full line) and the TPD reactivated one (dotted line). The observed trend is very similar for both samples with rather high conversions in the whole temperature range. There are only some slight differences in both  $\text{NH}_3$  and CO conversion at the highest temperatures, being a little bit more efficient the oxidation after reactivation. It is also worth to note that the experiments were conducted upon decreasing the reaction temperature and that the deactivation phenomenon was again only observed at 165 °C.

As a conclusion, it seems that the  $\text{NH}_4\text{NO}_3$  deposit leads to a pore blocking which affect the catalyst de- $\text{NO}_x$  efficiency by hindering

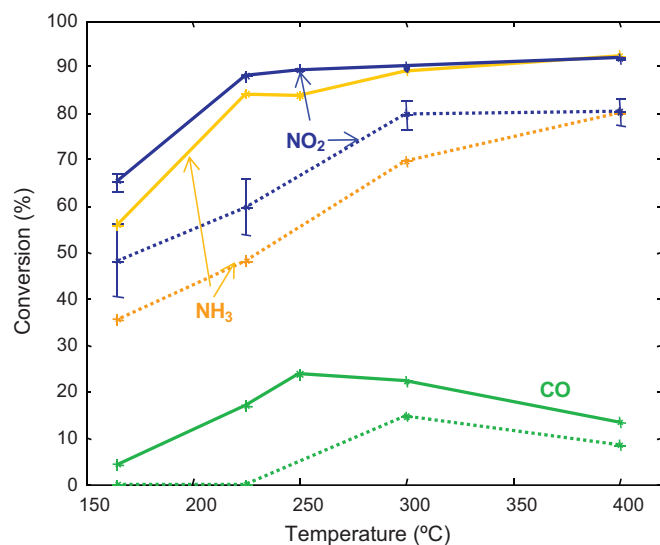


**Fig. 6.** Evolution of the conversion of NO<sub>x</sub>, NH<sub>3</sub> and CO with the temperature (NO<sub>2</sub>/NO<sub>x</sub> = 1 and NH<sub>3</sub>/NO<sub>x</sub> = 1.2) for both the "as received" aged sample (full line) and after TPD reactivation (dotted line).

the active sites accessibility. However, a single thermal regeneration, which simulates the catalyst real life upon changes of the engine regime conditions, occurring for example during a Diesel Particulate Filter (DPF) regeneration, leads to a full recovery of the catalyst SCR efficiency and no residual NH<sub>4</sub>NO<sub>3</sub> left on the surface (spectra not showed). This is an important point, since even if the formation of the ammonium nitrate deposit seems to be unavoidable during the cold start period, the NO<sub>x</sub> removal efficiency remains above 60% at a temperature as low as 165 °C and the further heating of the catalyst upon the increase of the engine load will lead to the deposit decomposition. For sure, this NH<sub>4</sub>NO<sub>3</sub> thermal decomposition is not selective to N<sub>2</sub> and various species (N<sub>2</sub>O, NO<sub>2</sub>, NH<sub>3</sub>) should be taken into account in the pollutant balance, however this decomposition will happen only during transient periods and interestingly will restore the sites accessibility, enabling the recovery of all the catalyst functions.

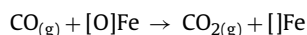
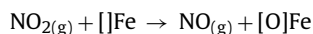
Finally, we must emphasize that we chose up to this point of the study to work with the aged catalyst which is more representative of an on-board working catalyst. However, it may be useful to gain information on the ageing effect on the SCR efficiency. For this purpose, the fresh catalyst was also tested in the range of temperatures between 165 °C and 400 °C with the same flow composition (150 ppm of NO<sub>2</sub> + 180 ppm NH<sub>3</sub> + 14% O<sub>2</sub> + 4% CO<sub>2</sub> + 300 ppm CO + 1% H<sub>2</sub>O). The results presented on Fig. 7, indicate that the same conversion line break takes place between 165 and 225 °C for both catalysts, which must be associated similarly to the NH<sub>4</sub>NO<sub>3</sub> induced deactivation. On another hand, it is also obvious from Fig. 7 that the aged catalyst possesses definitely better performances than the fresh one in the whole range of temperatures.

More specifically, it is worth noting that the aged catalyst is not only more efficient in deNO<sub>x</sub> than the fresh one, but it also leads to higher CO conversion thus suggesting a link between the CO conversion and the NO<sub>x</sub> removal activity. Indeed, we previously hypothesized from Fig. 2 that a gas phase reaction between CO and NO<sub>2</sub> could take place to yield CO<sub>2</sub> and NO, the later being further involved in the ammonia fast SCR path. However, in the rather low temperature range (200–300 °C) where the CO conversion is the highest, a pure gas phase reaction would be very slow and it's not detected in a blank. On the contrary, the catalytic oxidation of CO into CO<sub>2</sub> via  $\alpha$ -oxygen species present in similar Fe-ZSM-5 was



**Fig. 7.** Evolution of the conversion of NO<sub>x</sub>, NH<sub>3</sub> and CO with the temperature (NO<sub>2</sub>/NO<sub>x</sub> = 1 and NH<sub>3</sub>/NO<sub>x</sub> = 1.2) with the aged catalyst (full line) and the fresh catalyst (dotted line).

reported to significantly take place at temperature around 200 °C [44]. In this work from Bulushev et al., the active  $\alpha$ -oxygen species was described to be formed upon N<sub>2</sub>O decomposition onto iron red-ox active sites, however it was also observed recently for similar catalysts that the NO<sub>2</sub> adsorption at room temperature leads to the observation by infrared spectroscopy of (NO)<sub>ads</sub> and thus to the formation of the so called  $\alpha$ -oxygen species [45]. In the frame of the present study, the latest path would explain the formation of the active oxygen species able to convert CO into CO<sub>2</sub>; then the NO formed should participate with NO<sub>2</sub> in the fast SCR [46,47] and we can summarize the elemental steps as follows:



This proposal is consistent with a decrease of the CO conversion when pure NO was used as the NO<sub>x</sub> model molecule (see Fig. 2), since in this case the iron red-ox site is monopolized in the low temperatures range by the required NO to NO<sub>2</sub> oxidation. We must finally conclude from this part that the aged catalyst, being globally more efficient, would possess more active/available red-ox sites than the fresh one. It could mean that the ageing process led to iron oxidation within the zeolitic microporous system as reported by Ivanova et al. [48], although the ageing process was not the same.

### 3.2. Oxidation capacity of the catalysts

With the aim to understand some features of the de-NO<sub>x</sub> activities previously described, the NO and the NH<sub>3</sub> oxidation capacity of both catalysts were tested.

#### 3.2.1. NO oxidation

The standard SCR reaction is often described in the literature to be limited, for zeolite based catalyst, by the NO to NO<sub>2</sub> oxidation which is described to be the rate-determining step [24]. In order to further understand the NO oxidation capacity of the samples, a flow made of 1000 ppm of NO + 14% O<sub>2</sub> was sent to the catalysts at different temperatures. Fig. 8 illustrates, for the fresh catalyst, the typical IR spectra obtained from the gas phase analysis (the bands are assigned to gaseous NO and NO<sub>2</sub>). It is thus evident that as soon

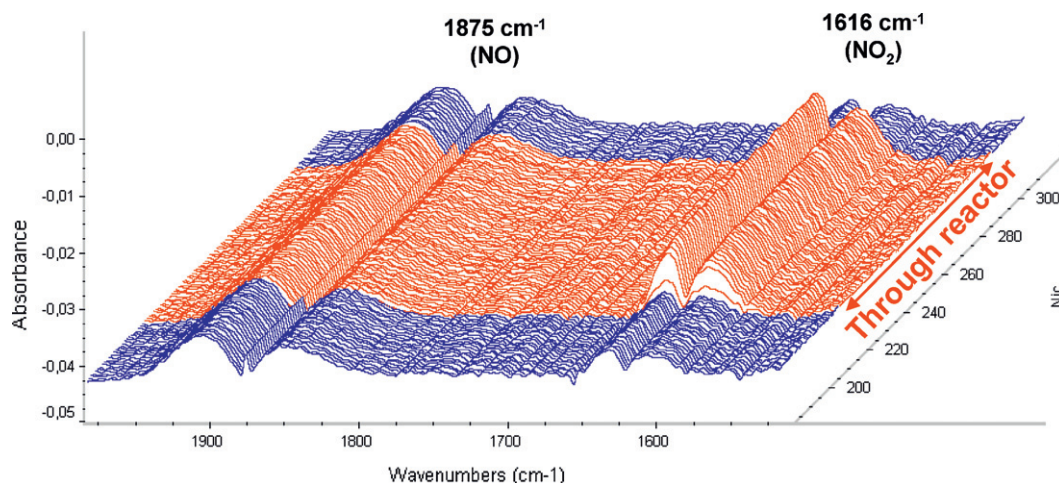


Fig. 8. Evolution of the IR gas-phase spectra during the NO to NO<sub>2</sub> reaction over the fresh catalyst at 300 °C.

as the gas flow is passing through the reactor where the catalyst lies, NO<sub>2</sub> is produced.

Regarding the quantities of NO converted to NO<sub>2</sub>, they were calculated for both catalysts in the whole temperature range and the results corrected from gas phase NO oxidation (estimated at around 5% ± 1 from a blank experiment) are given in Fig. 9. As expected according to both thermodynamic and kinetic considerations, the oxidation capacity for both fresh and aged catalyst increases with the temperature ( $\leq 400$  °C), but the ranking between catalysts changes with the tested temperature: at low temperature the oxidation capacity for the aged-catalyst is higher than for the fresh one, while at high temperature their behaviour is rather similar. This result may explain the higher CO oxidation capacity observed with the aged sample at temperatures below 300 °C (see Fig. 7).

Finally, in agreement with the literature data, the quite low oxidation capacity of both samples at low temperatures could effectively be a limitation for the SCR reaction when pure NO is present in the NO<sub>x</sub> flow. Indeed, the fact that for temperatures below 300 °C, the NO<sub>x</sub> conversion in pure NO SCR conditions is similar to the NO to NO<sub>2</sub> conversion (compare Figs. 1 and 9) suggests (considering

a rate order close to unity regarding NO in its oxidation reaction) that the NO to NO<sub>2</sub> would be the rate-determining step. Furthermore, the increase of the SCR (NO<sub>x</sub>-conversion) at low temperature, when pure NO<sub>2</sub> was used, together with the increasing CO conversion indicates that NO<sub>2</sub> interacts faster with the red-ox sites than NO does (see Fig. 2).

### 3.2.2. NH<sub>3</sub> oxidation

It is also of interest to study the NH<sub>3</sub> oxidation in order to better understand the differences observed between the NO and NH<sub>3</sub> conversion during the SCR tests. Indeed, in all cases a higher NH<sub>3</sub> consumption was found even if the stoichiometry of the reaction indicates a ratio NH<sub>3</sub>:NO = 1:1. The explanation of this phenomenon lies for sure in the parallel NH<sub>3</sub> oxidation from the oxygen molecules, so a deeper investigation was conducted and a flow made of 180 ppm of NH<sub>3</sub> and 14% of O<sub>2</sub> was sent to the fresh and aged catalysts at different temperatures.

The evolution of the gas phase NH<sub>3</sub> and of the adsorbed species formed on the catalytic surface during the experiment were analysed by IR (data not reported). Both NH<sub>4</sub><sup>+</sup> species and coordinated ammonia are formed on the surface of the catalyst upon time on stream and their amount reaches an “equilibrium” value when the steady state is established. Accordingly, the profile of the NH<sub>3</sub> concentration in the outlet gas is characterized at the beginning of the switch to the reactor by a decrease to the zero level (ammonia adsorption), however after few minutes the concentration increases and reaches a steady state level which was used for the estimation of the NH<sub>3</sub> oxidation capacity, as the difference between the fed ammonia and that measured at the outlet. The values of the NH<sub>3</sub> conversion (%) for each sample at different temperatures are given in Table 1. At high temperature the NH<sub>3</sub> oxidation by the catalysts is quite high; on the contrary at low temperature this reaction is negligible for both catalysts. The NH<sub>3</sub> oxidation is thus confirmed to be favoured by the catalysts in the high temperature range: in SCR conditions, part of the reducing agent will thus not be used for the SCR reaction being directly oxidized. This explains

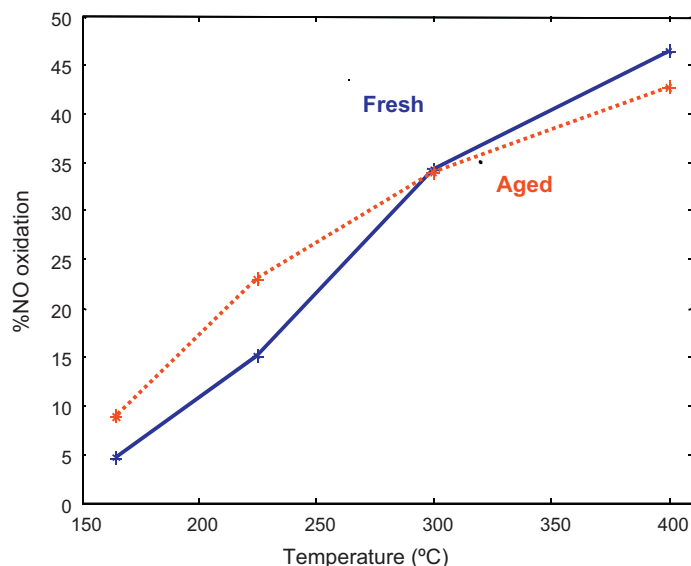


Fig. 9. Evolution of the NO oxidation capacity with the temperature when a flow of 1000 ppm NO + 14% O<sub>2</sub> is sent. Fresh catalyst (straight-line) and aged (dotted-line).

Table 1

Values for NH<sub>3</sub> oxidation conversion (in %) obtained for fresh and aged catalyst at several temperatures. Flow conditions: 180 ppm of NH<sub>3</sub> + 14% of O<sub>2</sub>.

T (°C)	Fresh	Aged
400	65	75
300	31	45
225	~0	~0
165	~0	~0



the limitation for the deNO<sub>x</sub> activity at high temperature: the NO<sub>x</sub> conversion never reaches 100% even with 20% excess of ammonia. It is also worth noting that no NO<sub>x</sub> species were detected neither by IR nor MS, implying that the ammonia oxidation from oxygen is N<sub>2</sub> selective according to the equation:  $2\text{NH}_3 + 3/2\text{O}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O}$  [35].

Finally, the comparison between the aged and the fresh catalyst again clearly indicates that the former possesses more efficient red-ox sites, in line with previous results.

In order to summarize the red-ox properties of the catalyst, we must remind that the aged sample always showed higher efficiencies than the fresh one whatever the involved oxidation reaction: CO to CO<sub>2</sub>, NO to NO<sub>2</sub> or NH<sub>3</sub> to N<sub>2</sub>. As the nominal amount of iron cannot increase during the thermal ageing at 750 °C in presence of 10% of H<sub>2</sub>O, one could suggest that either the accessibility of the red-ox active sites has been increased (upon partial framework deconstruction for example) or that the nature of the active sites changed to more efficient ones. Fejes et al. [49] reported that some iron sites can migrate in the electrostatic space of the zeolite structure after hydration and especially at elevated temperatures, forming a kind of “ferrihydrate” with the highest hydrogenation activity. Something similar could happen during the ageing process, but complementary experiments such as NO adsorption followed by IR at RT would be required to investigate qualitatively and quantitatively the evolution of iron species upon ageing, and this will thus be the object of a further article.

#### 4. Conclusion

The study of the ammonia SCR reaction with either pure NO or pure NO<sub>2</sub> (as NO<sub>x</sub> compounds) together with the deactivation of the catalyst by NH<sub>4</sub>NO<sub>3</sub> and its possible further regeneration was reported in this paper.

For temperatures below 300 °C, a marked NO<sub>x</sub> conversion increase was observed when using pure NO<sub>2</sub>, being over 50% in the whole temperature range for both the fresh and the aged catalysts.

Furthermore, even if the SCR efficiency was greatly enhanced with NO<sub>2</sub>, some residual NH<sub>3</sub> oxidation was still detected above 300 °C. For lower temperatures, and especially when pure NO<sub>2</sub> was used, the NH<sub>3</sub> oxidation part decreases. The NO<sub>2</sub> molecules possess a higher oxidizing power than NO; this result confirms that the main contribution to NH<sub>3</sub> oxidation does not take place in the gas phase and suggests that the NH<sub>3</sub> oxidation mechanism would go through co-adsorption of NO and NH<sub>3</sub> on the same (or neighbouring) oxidizing sites.

Going on with the use of pure NO<sub>2</sub> as the NO<sub>x</sub> species, it was observed from the surface data that for temperature as low as 165 °C, the IR spectra changed with prolonged time on stream, indicating an accumulation of species on the catalyst. The corresponding deposit was identified as ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) by complementary experiments. The formation of NH<sub>4</sub>NO<sub>3</sub> is thus provoked at low temperature by the presence of pure NO<sub>2</sub> and its deposit onto the catalyst was for the first time evidenced (to the best of our knowledge) by mean of the IR operando methodology. Its accumulation leads to a loss of activity for the NO<sub>x</sub> reduction, which must certainly be associated to the microporous system obstruction. Nevertheless, after a single thermal regeneration of the catalyst (which would arise during the catalyst ‘real life’ upon any increase of the engine regime), the SCR efficiency was fully recovered.

Furthermore, a comparison of the results for both fresh and aged catalysts when pure NO<sub>2</sub> was used indicates that the aged catalyst possesses definitely better de-NO<sub>x</sub> performances in the whole range of temperatures. A detailed look at the CO conversion levels (especially in the low temperature range) enabled to illustrate that

NO<sub>2</sub> favours the CO oxidation into CO<sub>2</sub> and thus that a highest SCR efficiency is reached when the CO conversion is high. In agreement with some literature data, this result suggests that NO<sub>2</sub> may dissociate onto the red-ox [Fe] sites to yield active α oxygen species [O]Fe and gaseous NO. The former species provides the active sites for CO oxidation into CO<sub>2</sub>, while nitrogen monoxide would participate in the fast SCR path (for which a stoichiometric mixture of NO and NO<sub>2</sub> is required). This result is quite important since it points out that a great care should be taken when comparing the literature data. More precisely, our high SCR efficiency when using pure NO<sub>2</sub> is a priori surprising since most of the literature data reports that the highest de-NO<sub>x</sub> level is reached for an equimolar mixture of NO and NO<sub>2</sub> for which the fast SCR operates. However, most of the literature data deals with a model flow made basically of NH<sub>3</sub>, NO<sub>x</sub> and O<sub>2</sub>, whereas H<sub>2</sub>O, CO<sub>2</sub> and traces of reducing agents such as unburnt HC's or CO are always present in the exhaust stream. Our results are indeed fully consistent with the general trend of the literature: the observed NO<sub>2</sub> assisted CO oxidation provides in situ the NO molecules required to reach the NO<sub>2</sub>/NO = 1 ratio, so that in the frame of this work we are dealing with a ‘masked’ fast SCR process.

Finally the oxidation capacity of both catalysts was also studied. At high temperatures, the selective NH<sub>3</sub> oxidation into N<sub>2</sub> by O<sub>2</sub> is relevant for both catalysts, which explains that the deNO<sub>x</sub> efficiency never reaches 100% even in the presence of an excess of ammonia. Regarding the NO to NO<sub>2</sub> reaction, the data show a quite low oxidation capacity for both samples at low temperature, which would limit the SCR reaction when pure NO is used. The fact that for temperatures below 300 °C the NO conversion in SCR conditions is similar to the NO to NO<sub>2</sub> conversion further indicates the NO oxidation as being the rate-determining step, indeed. A general comparison of the aged and fresh catalysts oxidation efficiencies finally allows us to conclude that the best catalysts regarding the SCR deNO<sub>x</sub> efficiency is the one for which the red-ox sites are the most active/abundant.

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